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Study of the Oxalate Ion Exchange Equilibria in Ion Exchange Resin Amberlite IRA-400

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The equilibrium constant in the standard state K_{std} for the uni-bivalent ion exchange between the resin (R) and the aqueous solution (aq)

$$2X^-_{(R)} + C_2O_4^{2-}(aq) \rightleftharpoons 2X^-_{(aq)} + C_2O^{2-}_{4(R)}$$

where $X^- = Cl^-$ or Br^- have been determined in anion exchange resin Amberlite IRA-400 with regards to mean activity coefficients of ions both in the solution and in the resin. The apparent equilibrium constant (k_{app}) for various equilibrium concentrations of $C_2O_4^{2-}$ in the solution have been calculated from the expression.

$$k_{app} = \frac{[C_{C_2O_4^{2-}(R)}][C_{X^-_{(aq)}\gamma^{\pm}_{(aq)}}]^2}{[C_{X^-(R)}]^2[C_{C_2O_4^{2-}(R)\gamma^{\pm}_{(aq)}}]}$$

The equilibrium constant in the standard state (k_{std}) is determined by a graphical method. The resin in its purely univalent anion form is chosen as the standard state. From k_{std} for vairous temperatures, the enthalpy change for the ion exchange reaction has been evaluated.

Key Words: Amberlite IRA-400, Oxalate ion, Exchange equilibria.

INTRODUCTION

In ion exchange reactions, the precise determination of the equilibrium constant in uni-bivalent in exchange has been found to be very difficult because of the lack of data on the activity coefficients of the ions in the ion exchange resin. The unavailability of these important data is a 'mising link' in the theory of ion exchange equilibrium[1]. Many workers[2-5] attempted the determination of such equilibrium constants but they all ignored the activity coefficients. Under such circumstances the best that can be done is to evaluate the equilibrium constant from experimental data or some logical basis. In present study we have evaluated the equilibrium constant for uni-bivalent ion exchange and the mean activity coefficient of the ions in the resin, $\gamma_{\pm(R)}$ on the basis of a certain chosen standard state for the two ion exchange reactions. Further, the enthalpy changes for these reactions have also been determined. As a typical case, the following two reactions have been studied in the strongly basic anion exchanger Amberlite IRA-400.

$$2Cl^{-}_{(R)} + C_2O_4^{2-}{}_{(aq)} \rightleftharpoons C_2O_4^{2-}{}_{(R)} + 2Cl^{-}_{(aq)} \quad (1)$$

$$2Br^{-}_{(R)} + C_2O_4^{2-}{}_{(aq)} \rightleftharpoons C_2O_4^{2-}{}_{(R)} + 2Br^{-}_{(aq)} \quad (2)$$

where (R) and (aq) represent the ion exchange resin and aqueous solution, respectively.

EXPERIMENTAL

The ion exchange resin supplied by manufacturer was in the chloride form and it was conditioned to remove impurities[6]. The resin was eluted with 5 % KCl followed by water to ensure that it was completely in chloride form. The resin in bromide form was obtained by eluting chloride form of the resin with ammonium bromide solution.

In a typical equilibrium study, 0.5 g of the resin in chloride form was mixed with 100 cm^3 of 0.01 M oxalic acid solution in narrow mouth reagent bottle and stoppered. Preliminary trials showed that the equilibrium was reached in *ca.* 24 h. Therefore the bottle was kept shaken for three hours and then kept for 24 h in thermostat. The concentrations of chloride ions in solution was estimated by potentometric titration with standard silver nitrate solution after 24 h. From this the amount of oxalate ions exchanged into the resin was estimated, since it is known that one mole of oxalate ion replace two moles of chloride ions. Because the initital concentration of oxalate ions and its amount of it which has exchanged into resin were known. The concentration of oxalate in the solution at equilibrium was calculated. Further, from the known resin capacity 1.27 mq per 0.5 g and the amount of oxalate ion replacing the chloride ion in resin, the amount of chloride ion remaining in resin was calculated.

From the concentration of chloride ion and oxalate ion in solution and the amount of chloride ion and oxalate ion in the resin at equilibrium the apparent equilibrium constant k_{app}, was calculated.

The same experiment was repeated with various concentration of the oxalate ion in the range of 0.006 to 0.050 M and each time apparent equilibrium constant was calculated (Table-1). The experiments were also carried out with the bromide form of the resin. The apparent equilibrium constant K_{app} in each case was calculated (Table-2).

The equilibrium constant were determined at various temperature in the range of 20 to 40ºC and the k_{std} at these temperatures were evaluated. From the plot of k_{std} *vs.* 1/T, the enthalpy change of the ion exchange reaction were determined (Tables 3 and 4).

TABLE-1
EQUILIBRIUM CONSTANT FOR THE UNI-BIVALENT ION EXCHANGE REACTION

$$2R\text{–}Cl + C_2O_4^{2-}{}_{(aq)} \rightleftharpoons R_2C_2O_4 + 2Cl^-{}_{(aq)}$$

Amount of the resin : 0.500 g; Volume of the $C_2O_4^{2-}$: 100 cm^3; Temp. : 25ºC

Initial conc. of $C_2O_4^{2-}$ (M)	Equilibrium concentration (M)		Amount of ion in the resin (meq/0.5 g)		$\sqrt{I}$	$\gamma_{\pm aq}$	k_{app}	$\gamma_{\pm R}$
	Cl^-	$C_2O_4^{2-}$	Cl^-	$C_2O_4^{2-}$				
0.006	0.0082	0.0019	0.450	0.410	0.118	0.758	35.8	0.743
0.008	0.0084	0.0038	0.430	0.420	0.141	0.719	21.1	0.437
0.009	0.0085	0.0047	0.420	0.425	0.150	0.704	18.3	0.379
0.010	0.0086	0.0057	0.410	0.430	0.160	0.688	16.5	0.342
0.015	0.0090	0.0105	0.370	0.450	0.201	0.624	12.7	0.263
0.020	0.0095	0.0156	0.390	0.475	0.237	0.574	9.1	0.189
0.030	0.0097	0.0255	0.370	0.485	0.293	0.503	6.5	0.135
0.050	0.0101	0.0452	0.330	0.505	0.382	0.408	5.3	0.109

TABLE-2
EQUILIBRIUM CONSTANT FOR THE UNI-BIVALENT ION EXCHANGE REACTION

$$2R\text{–}Br + C_2O_4^{2-}{}_{(aq)} \rightleftharpoons R_2C_2O_4 + 2Br^-{}_{(aq)}$$

Amount of the resin : 0.500 g; Volume of the $C_2O_4^{2-}$: 100 cm^3; Temp. : 25ºC

Initial conc. of $C_2O_4^{2-}$ (M)	Equilibrium concentration (M)		Amount of ion in the resin (meq/0.5 g)		$\sqrt{I}$	$\gamma_{\pm aq}$	k_{app}	$\gamma_{\pm R}$
	Br^-	$C_2O_4^{2-}$	Br^-	$C_2O_4^{2-}$				
0.008	0.0084	0.0038	0.430	0.420	0.140	0.720	21.0	0.573
0.010	0.0087	0.0057	0.400	0.435	0.161	0.686	17.4	0.475
0.015	0.0092	0.0107	0.420	0.460	0.203	0.621	10.3	0.281
0.020	0.0095	0.0156	0.390	0.475	0.237	0.574	9.1	0.249
0.030	0.0095	0.0253	0.320	0.475	0.292	0.504	8.3	0.227
0.050	0.0098	0.0450	0.290	0.490	0.381	0.409	6.6	0.180

TABLE-3
VARIATION OF EQUILIBRIUM CONSTANT IN STANDARD STATE FOR THE UNI-BIVALENT ION EXCHANGE REACTION

$$2R\text{–}Cl + C_2O_4^{2-}{}_{(aq)} \rightleftharpoons R_2C_2O_4 + 2Cl^-{}_{(aq)}$$

Amount of the resin : 0.500 g; Volume of the $C_2O_4^{2-}$: 100 cm^3

Temperature (ºC)	20	25	30	35	40
k_{std}	33.4	48.2	59.1	64.3	75.5

Slope of the plot of log k_{std} *vs.* 1/T = -1551.60
Enthalpy of the ion exchange reaction = 29.70 KJ mol^{-1}

TABLE-4
VARIATION OF EQUILIBRIUM CONSTANT IN STANDARD STATE FOR THE UNI-BIVALENT ION EXCHANGE REACTION

$$2R\text{–}Br + C_2O_4^{2-}{}_{(aq)} \rightleftharpoons R_2C_2O_4 + 2Br^-{}_{(aq)}$$

Amount of the resin : 0.500 g; Volume of the $C_2O_4^{2-}$: 100 cm^3

Temperature (ºC)	20	25	30	35	40
k_{std}	30.0	36.6	43.3	47.0	57.3

Slope of the plot of log k_{std} *vs.* 1/T = -1232.43
Enthalpy of the ion exchange reaction = 23.59 KJ mol^{-1}

RESULTS AND DISCUSSION

The equilibrium constant for the ion exchange eqns. 1 and 2 can be represented by the expression

$$k = \frac{[a_{C_2O_4^{2-}(R)}][a_{X^-_{(aq)}}]^2}{[a_{X^-(R)}]^2[a_{C_2O_4^{2-}(R)}]}$$

where the a is the activities of the ions and X^- = Cl^- or Br^-. Here the activities of the X^- and Y^- in the aqueous solutions are obtained from their respective concentrations and activity coefficient derived from Debye-Huckel limiting law[7]. With regards to the activities of the two ions in the resin are concerned, the situation is different. Ordinarily the activity should be obtained as a product of the concentration and the activity coefficient. In lieu of the concentration of the ions in the resin, their respective amount in milliequivalent can be used. On this basis, the equilibrium constant would be given by the expression

$$K = \frac{(C_{R2C_2O_4^{2-}} \cdot \gamma_{R2C_2O_4^{2-}})(C_X \cdot \gamma_X)^2}{(C_{RX} \cdot \gamma_{RX})^2 (C_{2C_2O_4^{2-}} \cdot \gamma_{2C_2O_4^{2-}})}$$

In this expression, the concentration of ions in the resin in terms of their amounts in milliequivalent are known while their indvidual activity coefficient *i.e.* γ_{RX} and γ_{R2X} are not known. Indeed, it appears that there is no way of evaluating them individually. Also the activity coefficients can not be ignored because in the expression for equilibrium constant they appears as $(\gamma_{R2C_2O_4^{2-}})/(\gamma_{RX})^2$.

Since $\gamma_{R2C_2O_4^{2-}}$ and γ_{RX} are likely to vary with the concentrtion of the ions X^- and $C_2O_4^{2-}$ in the resin, the above mentioned quantity is also likely to vary with the concentration of the ions in the resin. This is evident from the fact that the equilibrium constant as calculated from the expression

$$k_{app} = \frac{(C_{R2C_2O_4^{2-}})(C_X \cdot \gamma_X)^2}{(C_{RX})^2 (C_{2C_2O_4^{2-}} \cdot \gamma_{2C_2O_4^{2-}})}$$

various with concentration of the ions in the resin (Tables 1 and 2).

In absence of any method to determine the activity coefficient of the ions in the resin individually the best that can be done is to attempt to determine the quantity $(\gamma_{R2C_2O_4^{2-}})/(\gamma_{RX})^2$ and to determine the true equilibrium constant.

It is best to choose the ion exchange resin capacity in the univalent form or standard state and refer the resin at any other composition of the uni/bivalent ion to this stand state. Therefore the apparent equilibrium constants calculated by the above equation have been plotted versus the equilibrium concentrations of the oxalate ion in the solution. Extrapolating this curve to zero equilibrium concentration of $C_2O_4^{2-}$ ion in the solution, one obtains the equilibrium constant in solution, k_{std}. Having thus obtained the equilibrium constant in the standard state one can obtain the activity coefficient ratio of ions $(\gamma_{R2C_2O_4^{2-}})/(\gamma_{RX})^2$ at any finite equilibrium concentration of $C_2O_4^{2-}$ ion in the solution as the ratio of k_{app}/k_{std}. (Tables 1 and 2).

By plotting log k_{std} *vs.* 1/T, one obtains a satisfactory straight line, from the slope of which the enthalpy change and the ion exchange reaction is determined (Tables 3 and 4).

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